POTASSIUM-ARGON DATING OF IGNEOUS ROCKS IN PENDLETON COUNTY, WEST VIRGINIA

A Thesis

Presented in Partial Fulfillment

of the Requirements for the

Degree Bachleor of Science

by

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INTRODUCTION

The igneous rocks analyzed in this study came from southeast Pendleton County, West Virginia, near the town of Sugar Grove (Fig. 1). Pendleton County, in the east central part of the state lies in the Valley and Ridge physiographic province. The topography here is rugged (Figs. 2, 3) going from 4862 feet on Spruce Knob, in the central part of the county, to 1155 feet at the South Branch River level on the Pendleton-Grant County line, or a difference in elevation of 3707 feet. Fig. 4 shows the topography and location of igneous rocks in this area.

The rocks of Pendleton County, with the exception of these igneous intrusions, are all Paleozoic sediments ranging in age from Ordovician to Early Pennsylvanian. The igneous rocks are found only in sediments of Devonian age or older. The Brallier (Portage) shale on the east flank of the Stone Mountain Anticline contains most of the exposures of igneous rocks. Garnar (1956) believes this is due to well-developed joints in the shale which made it possible for the magma to find zones of weakness along which to ascend. Fig. 5 shows the geologic setting of southeastern Pendleton County.

K-Ar age determinations were made on one whole rock basalt sample and one biotite separation to see if these rocks were time related to other igneous rocks in Highland and Augusta Counties, Virginia.

ACKNOWLEDGMENTS

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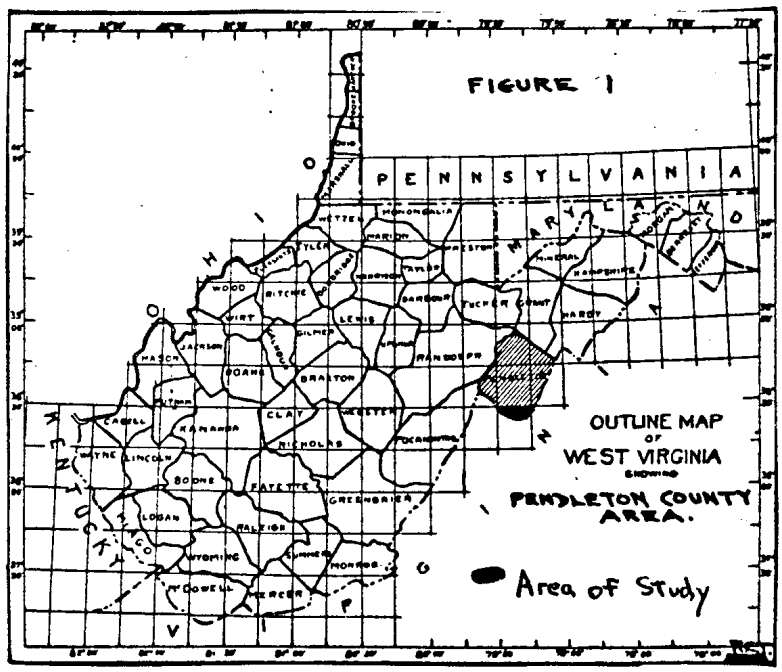
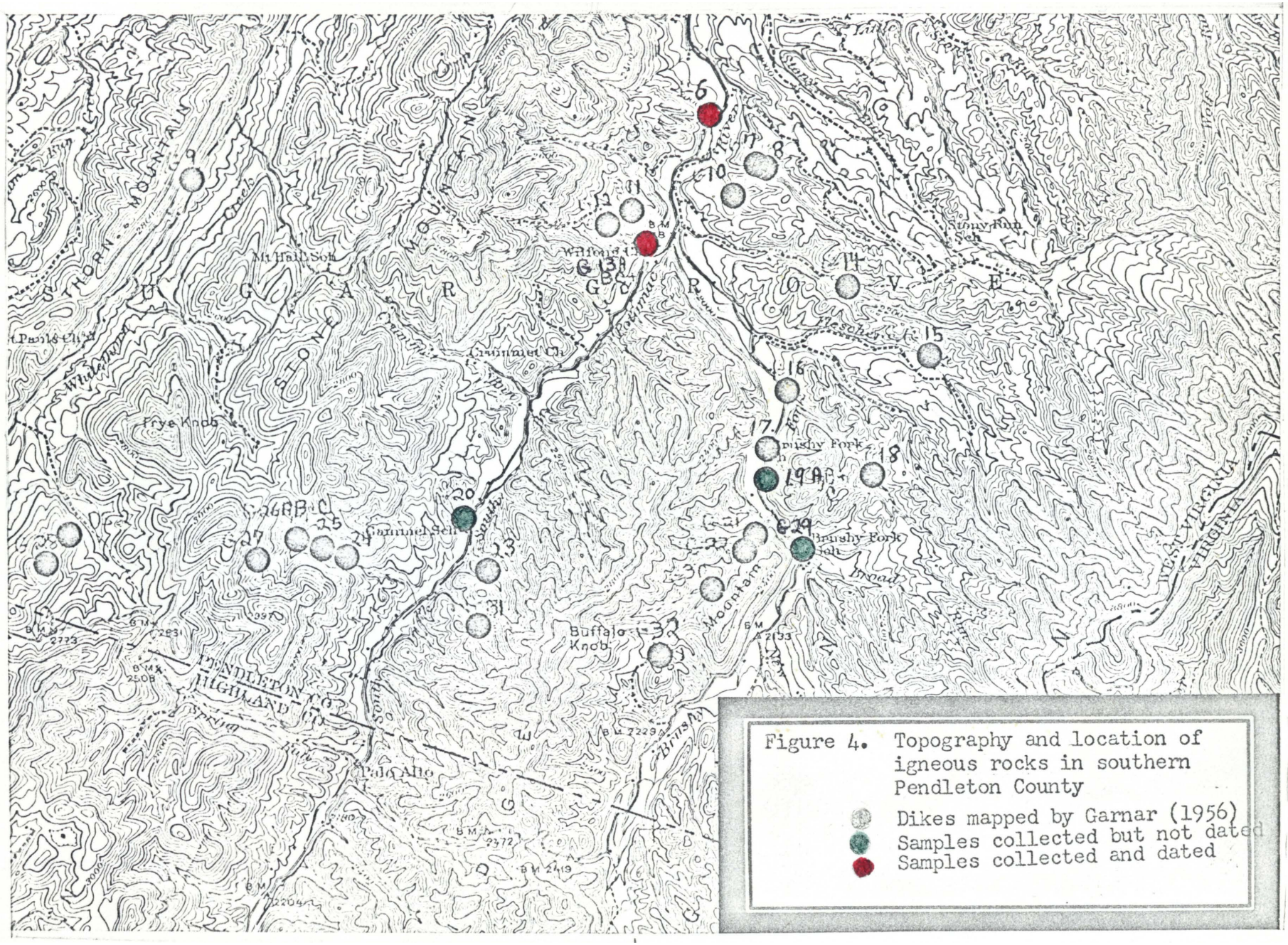


FIGURE 1
PENNSYLVANIA
OUTLINE MAP
OF
WEST VIRGINIA
SHOWING
PENDLETON COUNTY
AREA.
Area of Study

Figure 2. Southern Pendleton County as seen from an overlook on U. S. Route 33.

Figure 3. Germany Valley, southern Pendleton County, as seen from U. S. Route 33.


STONY MOUNTAIN
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Williams Ch
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Fleschers Ch
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Brushy Fork Sch
Mountain
Buffalo Knob
Pale Alto
PENDLETON HIGHLAND
WEST VIRGINIA
VIRGINIA
Figure 4. Topography and location of igneous rocks in southern Pendleton County
Dikes mapped by Garnar (1956)
Samples collected but not dated
Samples collected and dated

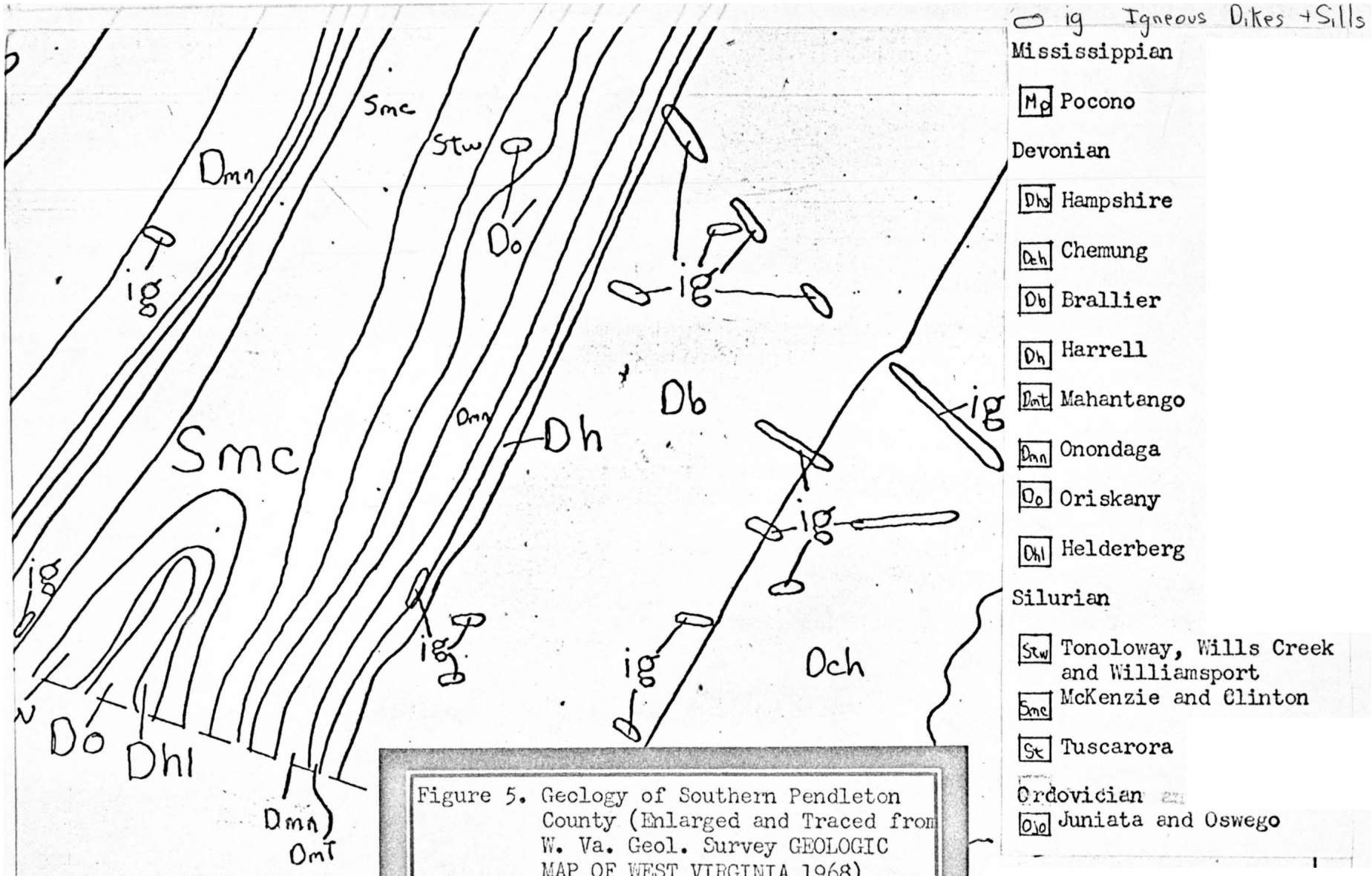

Figure 5. Geology of Southern Pendleton County (Enlarged and Traced from W. Va. Geol. Survey GEOLOGIC MAP OF WEST VIRGINIA 1968)

IGNEOUS ROCKS

Forty-seven exposures of igneous rocks are known in southeastern Pendleton County. Of these, one was mapped by Darton (1894), three by Woodward (1943, 1949), and forty-three by Garnar (1956). Garnar classifies these exposures as:

Andesite	1 exposure
Olivine-free basalt	23 exposures
Altered olivine basalt	5 exposures
Diabase	1 exposure
Mica basalt porphyry	1 exposure
Hornblende basalt	1 exposure
Olivine basalt porphyry	1 exposure
Volcanic breccia	4 exposures
Peridotite porphyry	2 exposures
Mica pyroxenite	4 exposures
Albitite	2 exposures
Altered dike rock	2 exposures

During the winter of 1970 this author collected samples from eight of these intrusions. Of the eight, six, which will be briefly discribed, were unsuitable for dating. The remaining two were dated and will be discussed at length later.

Dikes G1A and G1B, both peridotite porphyry, are located along US Route 33, three-quarters of a mile west of the summit of South Fork Mountain and several miles north of the other dikes. For this reason, they are not shown on the maps. G1A is two feet wide and strikes N30° W and dips 90° while G1B is one foot wide and strikes N24° W and dips 90°. Both are easily identified because they weather much faster than the surrounding hard Juniata sandstone (Fig. 6), and are therefore indented into the road cut. No fresh rock could be found at G1B and only two small pieces could be found at G1A. These specimens, because of the high degree of alteration, were unsuitable for dating.

Dike G2 and sill G20 are olivine-free basalts. Dike G2 is found on the north side of US Route 33 two miles west of the West Virginia-Virginia border and north of the area of Fig. 4. It is about five feet wide and strikes due west with a dip of almost 90°. The samples collected here were badly altered and contained zeolites and thus were not suitable for dating. Sill G20 is the only sill studied in Pendleton County.

It is found in a road cut near the former site of Gammel School. The termination of the sill to the north is very abrupt and can easily be seen. The sill weathers less readily than the surrounding shale and therefore the area underlain by the sill is fifteen feet higher than the area to the north where the sill is absent. The specimens taken from this road cut were fresh, but contained many vesicles filled with zeolites which made the samples unsuitable for dating.

Dike G29 is composed of albitite and is located in a stream bed just across the road from the old Brushy Fork School. It is over one hundred and fifty feet thick and strikes N85 E with unknown dip. The fresh samples of this rock looked like a white sandstone, but thin sections showed that the feldspar was altered and thus unsuitable for dating.

Dike G19A, an olivine basalt porphyry, is located one thousand feet upstream from Brushy Fork Church. According to Garnar (1956) it cuts a dike of olivine-free basalt. The basalt dike could not be located by this author because of high water in the stream. Dike G19A is five feet thick, and strikes N60 W with a dip of 90 . This section revealed lack of a suitable mineral for dating along with a small amount of calcite.

G6 and G13A were the two dikes chosen for age analysis. G6 is a mica pyroxenite, is twelve to fourteen feet wide, and strikes N33 W with a dip of 90 . It is located in a road cut on the west side of the road, 1.9 miles south of Sugar Grove. It is easily recognized, standing several feet above the surrounding softer shale (Fig. 7). The rock is made up of 30% pyroxene, 15% biotite, and 5% magnetite set in a groundmass which makes up 50% of the rock. No mineral identification of the groundmass was made. There are also very small traces of calcite, zeolites and pyrite.

The rock is very fine grained with an occassional large phenocryst of biotite. Several xenoliths were noted at the outcrop, but the samples for dating were collected as far away from these as possible. The samples were examined very thoroughly after crushing and before grinding to be sure no xenoliths were present. It was decided that biotite, because of its fresh appearance and quantity would be used

Figure 6. Dike G1B

Figure 7. Dike G6

for dating.

Dike G13A, a diabase located just south of Wilfong Church in a road cut (Fig. 8), is over one hundred feet wide, strikes N55 W and dips 90 . It is hard to recognize because of the weathered appearance of the outcrop. The rock weathers to a light brown on the outer surface, but is dark gray to black when fresh. Despite the weathered appearance of the outcrop, sufficient fresh rock was found for dating. The rock consists of 85% labradorite, which occurs in large laths. The remaining 15% consists mainly of augite with small traces of zeolites, serpentine, and biotite. Because of the large amount of fresh plagioclase and small amount of other minerals, this sample was run using the whole rock method.

AGE DETERMINATION

The decay of K^{40} is a branching decay (Fig. 9). K^{40} decays to Ca^{40} by β^- emission and conversion of a neutron to a proton. Attempts have been made to use the decay of K^{40} to Ca^{40} for dating, but because of the trouble of telling original Ca^{40} from radiogenic Ca^{40}, the method is subject to large errors. The decay of K^{40} to Ar^{40}, the basis for K-Ar dating takes place by three different methods: 1) by electron capture when an electron falls into the nucleus and unites with a proton to form a neutron. When this happens, the argon atom is in an excited state and quickly decays to ground state by emission of a gamma ray. 2) a small percentage of the argon that decays by the above method goes directly to ground state without emission of a gamma ray. 3) by emission of a positron. This is very rare and Dalrymple and Lanphere (1969) state that only .001% of K^{40} decays this way.

Radioactive decay is a statistical process in which the number of atoms that disintegrate per unit time, -dN/dt, is proportional to the number of atoms present, N. Thus

$$-\frac{dN}{dt} = \lambda N$$

Figure 8. Dike G13A

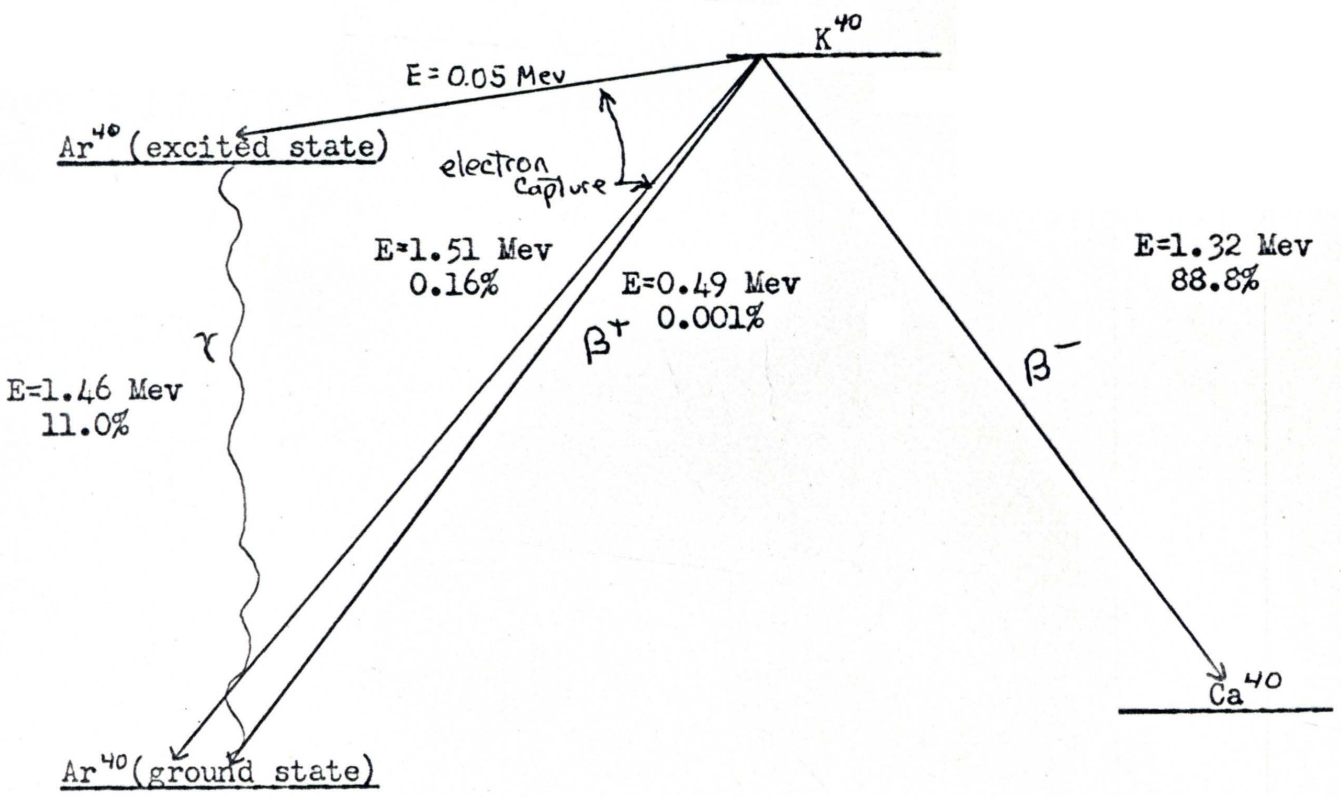

Figure 9. Branching Decay of K^{40}. Also indicated are the energy, E, released in each mode of decay and the $\%K^{40}$ that decays by each mode. (Dalrymple and Lanphere, 1969)

where λ, the decay constant, represents the probability that an atom will decay in unit time.

If equation (1) is integrated between $N=N_0$ at $t=0$ and $N=N$ at $t=t$ we get

$$\int_{N_0}^{N} \frac{dN}{N} = -\int_{0}^{t} \lambda dt, \tag{2}$$

$$\text{Log}_e \frac{N}{N_0} = -\lambda t, \tag{3}$$

$$N = N_0 e^{-\lambda t}, \tag{4}$$

which is the basic radioactive decay formula; N_0 is the initial number of atoms present and N is the number of atoms at time t.

If no parent or daughter atoms are lost or gained by the system, then the rate of decrease of the parent atoms equals the rate of increase of the daughter atoms, D.

$$\frac{dD}{dt} = -\frac{dN}{dt} \tag{5}$$

Thus, at any given time,

$$N_0 = N + D \tag{6}$$

Substituting equation (6) into equation (4) we get

$$D = N(e^{\lambda t} - 1) \tag{7}$$

For branching decay with two daughter products, D_1 and D_2, the formula becomes

$$D_1 + D_2 = N[e^{(\lambda_1 + \lambda_2)t} - 1] \tag{8}$$

For the decay of K^{40} this is

$$Ar^{40}_{rad} + Ca^{40}_{rad} = K^{40}[e^{(\lambda_\epsilon + \lambda_\beta)t} - 1] \tag{9}$$

where λ_ϵ is the decay constant for the K^{40}-Ar^{40} branch and λ_β is the decay constant for the K^{40}-Ca^{40} branch.

The decay constants used in this study are those suggested by Aldrich and Wetherill (1958). They correspond to activities of natural potassium of 3.4γ/gram sec and

27.6 γ/gram sec and are

$$\lambda_\epsilon = 0.585 \times 10^{-10}/\text{yr.} \tag{10}$$

and

$$\lambda_\beta = 4.72 \times 10^{-10}/\text{yr.} \tag{11}$$

The total decay constant is

$$\lambda = \lambda_\epsilon + \lambda_\beta = 5.305 \times 10^{-10}/\text{yr.} \tag{12}$$

The ratio of Ar^{40} to Ca^{40} produced by the decay of K^{40} is called the branching ratio, R, where

$$R = \frac{\lambda_\epsilon}{\lambda_\beta} = 0.124 \tag{13}$$

because this is the ratio of the daughter atoms,

$$R = \frac{D_1}{D_2} \quad \text{or} \quad D_2 = \frac{D_1}{R} \tag{14}$$

Solving equation (8) for t we get

$$t = \frac{1}{\lambda_1 + \lambda_2} \log_e \left[\frac{N + D_1 + D_2}{N}\right] \tag{15}$$

Substituting $\lambda = \lambda_1 + \lambda_2$ and $\frac{D_1}{R}$ for D_2,

$$t = \frac{1}{\lambda} \log_e 1 + \left[\frac{D_1 (1 + \frac{1}{R})}{N}\right] \tag{16}$$

Substituting the values for λ and R, equation (16) becomes

$$t = 1.885 \times 10^9 \log_e \left[9.068 \frac{D_1}{N} + 1\right] \quad \text{or.} \quad t = 1.885 \times 10^9 \log_e \left[9.068 \frac{Ar^{40}_{rad}}{K^{40}} + 1\right] \tag{17}$$

which is the potassium-argon age equation.

There are five assumptions made whenever the above equation is used to calculate ages. They are: 1) the decay of K^{40} takes place at a constant rate, regardless of its chemical or physical environment. 2) the present-day proportion of K^{40} to K_{Total} is the same in all materials to which the potassium-argon method is applied. 3) all argon in the rock or mineral is either radiogenic or atmospheric; that is, there is no extraneous argon. 4) The rock or mineral has been a closed system since t ; that is, there has been no loss or gain of K^{40} or Ar^{40} except for that which results from the

radioactive decay of K^{40}. 5) The time of formation of the rock or mineral is short compared to its age.

SAMPLE PREPARATION

Samples large enough for K-Ar analysis were collected from dikes G1A, G1B, G2, G6, G13A, G19A, G20, and G29. Several thin sections were made of all of these. Examination of the thin sections showed that only G6 and G13A were suitable for K-Ar analysis. Of these two, it was decided that G13A should be run as a whole rock, while G6 would be a biotite separation. Dike G6 contained from 10-20% biotite.

The whole rock sample of dike G13A was prepared by cutting a $1\frac{1}{4}'' \times \frac{3}{8}'' \times \frac{3}{8}''$ piece from the hand sample with a diamond saw. Pieces about $\frac{1}{8}''$ thick were cut from both ends. The three pieces were then washed in distilled water, dried in an oven, and put into a desiccator overnight. The two small end pieces, to be used for potassium analysis, were then crushed in a mortar and put through a 100 mesh sieve. The larger piece, now about $\frac{2}{3}'' \times \frac{3}{8}'' \times \frac{3}{8}''$ was used for argon extraction.

About five pounds of rock from dike G6 was crushed and sieved. Because of the small grain size and the problem of combined grains, it was decided to use 60-100 mesh for further purification. This sample was then washed to get rid of unwanted dust and dried in an oven. The heavy minerals, including biotite, were then separated by the use of bromoform , specific gravity 2.88. After being dried again, the magnetite was extracted with a hand magnet. The sample was then papershaken and handpicked to obtain the purest possible separation.

POTASSIUM ANALYSIS

Two splits were made of both the powdered whole rock sample and the biotite separate with each split weighing about .1 gram. The four samples were then dissolved in sulfuric and hydrofluoric acids and heated overnight to drive off silicon and fluorine by evaporation. Unwanted iron and other elements are precipitated as unsoluble sulfates and carbonates and carefully filtered out. This leaves the final solution containing the alkali metals and magnesium to which the lithium standard is added.

Great care must be taken in the preparation of the solution or large errors will result. Errors can result from loss of solution, contamination, or bad readings on the flame photometer. The solution is now ready for the flame photometer(Figure. 10).

All elements emit a characteristic radiation when excited. This occurs when an electron in the atom of the element falls from a higher to a lower energy level. The wavelength of the emitted light is inversely proportional to the difference in energy of the two levels, while the amount of the element present is directly proportional to the intensity of the radiation. Most elements require very high temperatures to excite the atoms, but the alkali metals need only to be burnt in a propane-air flame. The flame photometer uses these properties and compares the emission of an unknown sample with that of two known standards, one of lower potassium concentration and one of higher potassium concentration. The potassium concentration of the unknown is then found by linear interpolation.

The lithium internal standard technique of flame photometry is the one used in the O. S. U. laboratory. In this technique a small quantity, 25 ml., of a lithium internal standard containing 2000 ppm. lithium is added to both the known and the unknown. The solution is atomized in the burner flame. The light path of the radiation is then put through a filter and into a photomultiplier cell. The reading from the photomultiplier cell is put on a meter and is proportional to the concentration of potassium in the solution. Once the concentration of potassium in the solution is found, it is easy to calculate the percent of potassium in the sample from the concentration and the weight of the sample.

ARGON ANALYSIS

The O. S. U. K-Ar laboratory used the Berkeley method of argon extraction and purification (Fig. 11). The two samples are weighed out and placed in molybdenum crucibles. The crucible containing the biotite is covered with a lid to keep the grains from flying out. The crucible is sealed in a sample bottle and joined to the extraction line. A tracer and sample take-off tube is also joined to the line. The whole line

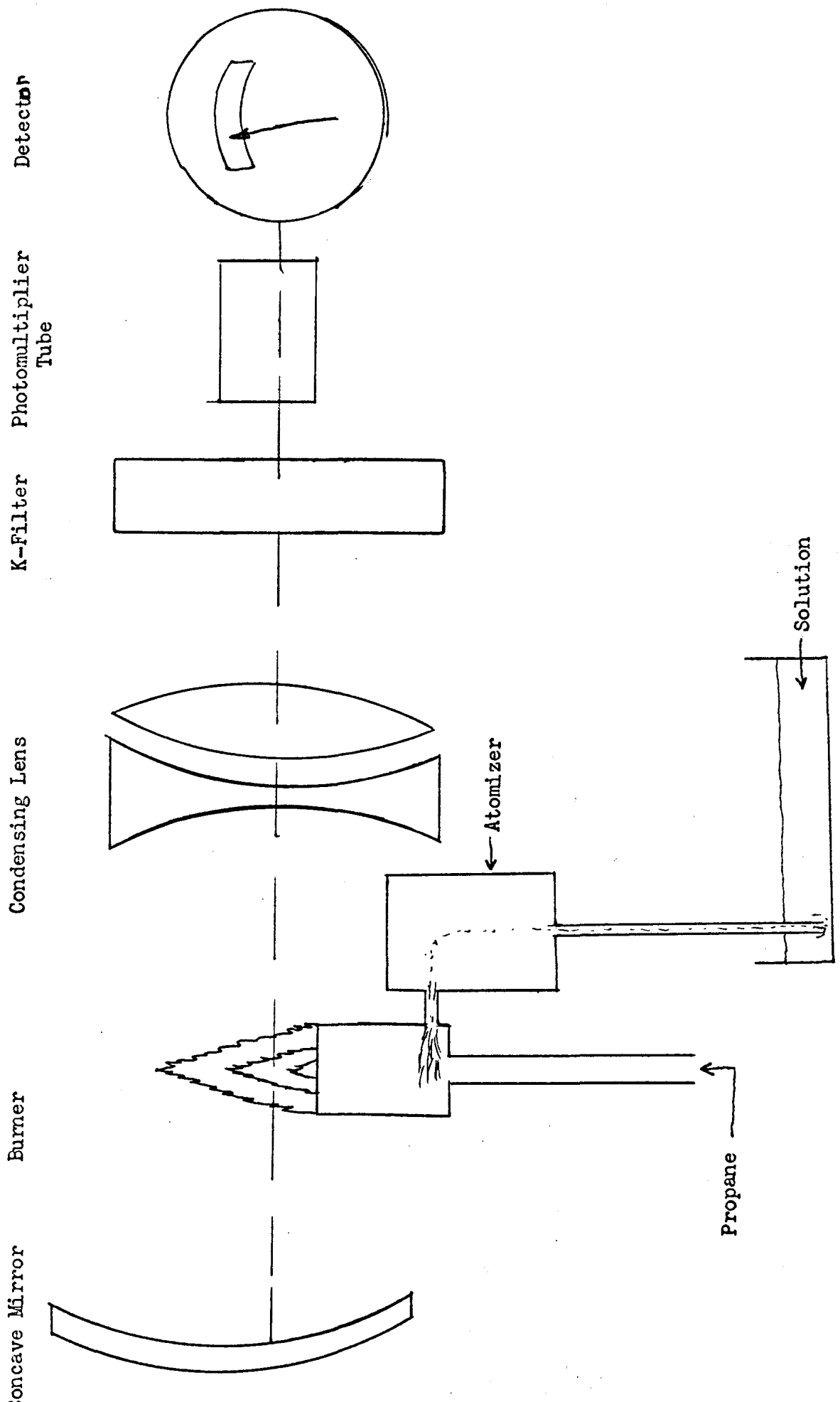

Figure 10. Diagram of the Zeiss PF-5 Flame Photometer

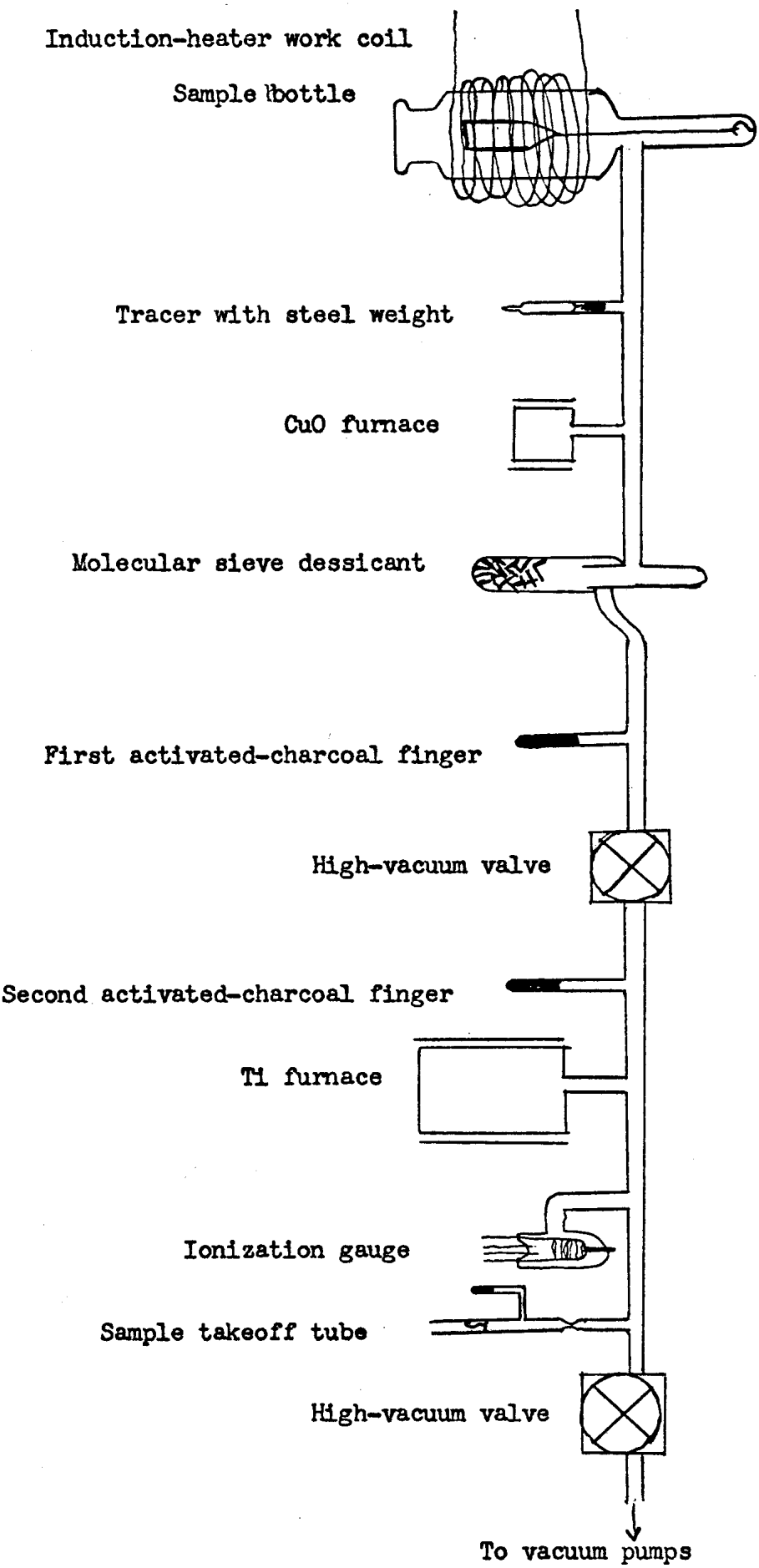

Figure 11. Diagram of the argon extraction and purification system. (Dalrymple and Lanphere, 1969)

is baked overnight, after which the pressure is ususally around 10^{-7} torr. The extraction line is then isolated from the pumping system by closing a valve. An induction heater coil is then placed around the sample bottle and the sample is fused. The coil induces a current flow in the crucible and thus heats the crucible without heating the sample bottle. The bottle, however, is heated by radiation from the crucible and has to be cooled with a fan. While the fusion is going on a tracer containing a known amount of Ar^{38} with small quantities of Ar^{36} and Ar^{40} is released by a weight, pulled up by a magnet, and dropped on the break-off tip. The gas liberated by the fusion is collected on the first activated charcoal finger which is cooled to the temperature of liquid nitrogen (-196 C). When the fusion is done and the sample bottle cool, the gas is released by warming the charcoal finger. This gas is exposed to a mizture of Cu and CuO at a temperature of 450° to 550° C. Hydrogen is oxidized to water and hydrocarbons are oxidized or burnt. Water is absorbed by the synthetic molecular sieve. After 20 minutes the line is tested with a Tesla coil to be sure all the water has been absorbed. Once all the water is gone the gas is transferred to the section of the line between the valves, using a second activated charcoal finger cooled in liquid nitrogen. The valve is closed, the finger warmed, and the gas exposed to Ti metal at 800° C. The Ti removes all but the inert gases, which are then collected in a sample take-off tube by using a third smaller activated charcoal finger. The take-off tube is then removed with a blowtorch. The sample is now ready for the mass spectrometer(Figure 12)

The mass spectrometer used at the O. S. U. laboratory is the Nier type. It is a first-order direction-focusing spectrometer with a 60° magnetic deflection and 6 inch radius of curvature. It is made of stainless steel and is operated in the static mode. The ion source is the filament type which uses a filament to produce electrons which then bombard the gas atoms as they enter the ionization chamber. The energy of the electrons used for ionization should be kept around 50 volts in order to minimize the number of multiply charged ions and maximize the number of singly charged ions. The

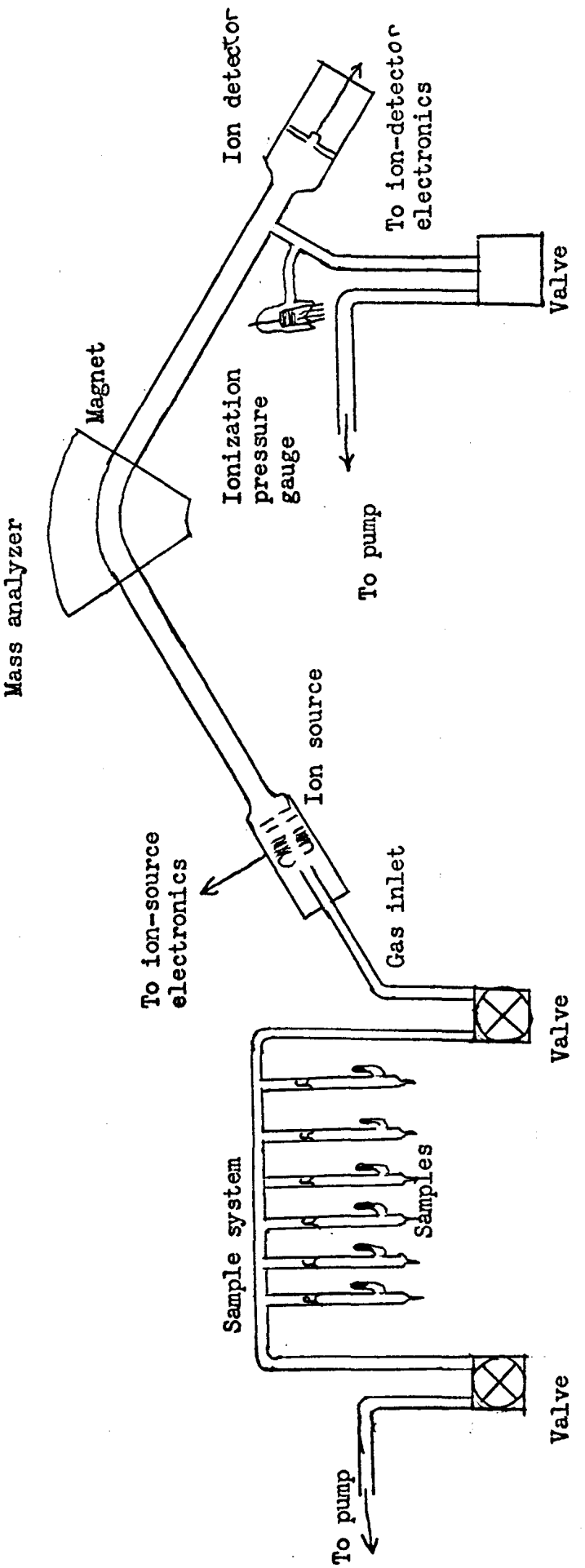

Figure 12. Diagram of a Nier-type mass spectrometer. (Dalrymple and Lanphere, 1969)

ions thus formed are accelerated by a difference of 3000 volts between the ionization chamber and the source-object slit. As the ion beam passes through the magnetic field, the ions are deflected into circular paths, the radii of which are inversely proportional to the square root of e/M, where e is the charge of the ion and M is the mass. The ion beams are then measured by a simple cage-type ion collector, which in turn is attached to an amplifier known as a vibrating-reed electrometer. The electrometer is then connected to a strip chart.

Twelve sweeps were made with the spectrometer. The Ar^{40} peak was recorded first, then the Ar^{38}, and finally the Ar^{36}. Times were marked off on the chart and peak heights from the base lines were measured. This information was then entered into the computer along with the potassium analysis. The computer calculated the spectrometer readings at t 0, and then calculated the amount of argon present by use of the isotope dilution formula

$$Ar^{40}_{rad} = Ar^{38}_{T} \left\{ (Ar^{40}/Ar^{38})_M - (Ar^{40}/Ar^{38})_T - \left[\frac{1-(Ar^{38}/Ar^{36})_M (Ar^{36}/Ar^{38})_T}{(Ar^{38}/Ar^{36})_M (Ar^{36}/Ar^{38})_A - 1} \right] \right.$$

$$\left. \left[(Ar^{40}/Ar^{38})_A - (Ar^{40}/Ar^{38})_M \right] \right\} \quad \text{where}$$

Ar^{40}_{rad} = atoms of radiogenic Ar^{40} in sample

Ar^{i}_{T} = atoms of isotope i in tracer

Ar^{i}_{A} = atoms of isotope i in atmospheric contaminant

Ar^{i}_{M} = atoms of isotope i in mixture

(For derivation of this formula see Dalrymple and Lanphere (1969))

Table 1. Results

Sample No.	%K^+	Ave. %K^+	% Difference K^+	Moles Ar^{40}/Gm.	Ar^{40}/K^{40}	% Rad. Ar^{40}	% Standard Deviation	Age	Standard Deviation
G6	6.112 6.080	6.096	.512	1.644×10^{-9}	8.861×10^{-3}	91.8	1.17	145.7×10^{6} yrs.	1.7×10^{6} yrs.
G13A	1.178 1.209	1.193	2.59	9.026×10^{-11}	2.486×10^{-3}	35.2	4.95	42.0×10^{6} yrs.	2.1×10^{6} yrs.

DISCUSSION AND CONCLUSIONS

Until the early 1960's, the final period of igneous activity in eastern North America was considered to be Triassic. However, since then age determinations on igneous rocks from Quebec, Vermont, New York, Virginia, and now West Virginia show that igneous activity occurred into Jurassic, Cretaceous, and Eocene time (Fairbairn and others, 1963; Zartman and others, 1967; Fullagar and Bottino, 1969). Fullagar and Bottino (1969) obtained a date of 47 million years on felsite intrusions 20 miles to the south-southwest of Sugar Grove. This is slightly older than the 42 million year date of the diabase dike, G13A. The 146 million year date of the mica pyroxenite, G6, corresponds very well to the 150 million year age obtained by Zartman and others (1967) on a nepheline syenite dike 40 miles south east of Sugar Grove. It appears that during both Jurassic and Eocene time igneous activity started outside Pendleton County and migrated northwest during Jurassic time and north-northeast during Eocene time and reached Pendleton County about 5 million years later.

Zartman and others (1967) have suggested that Pendleton County lies along the eastern extension of the 38th parallel fracture zone. Fullagar and Bottino (1969) concluded from the initial Sr^{87}/Sr^{86} ratio (0.704) that the intrusions in Highland County, Virginia originated in a magma chamber in the lower crust or upper mantle. Dennison and Johnson (1971) showed that a deep solidified pluton may be located under east-central West Virginia and west-central Virginia. Dennison and Johnson also show that igneous activity in this eastern section of the 38th parallel fracture zone has been sporadic for more than .8 billion years and may still be a zone of deep crustal weakness.

The dates of 42 and 146 million years on dikes in Pendleton County, West Virginia show that this area lies at the intersection of two sets of dikes of very different ages. This could explain the large concentration of dikes in southern Pendleton County.

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